[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK. Good afternoon. So what have we done so far? What is thermodynamics about? Remember you told us that it's about heat and work. But to date, we haven't defined heat yet, or we spoke about work, although indirectly, with the weight processes.

But we have done four hours, and we'll do another two today without talking about heat. Not saying that thermodynamics is not about heat. It is also about heat. But you can go a long way without and before defining the heat interaction, which will be in the topic of next lecture on Friday.

So how could we go that long, all right? We just review briefly what we've done. We define a few words, like system, property, state, what we mean by law or principle, which is, in fact, a theorem of the equation of motion of your model. Then we introduced the first law, which is a statement of existence, or actually, the first assertion is a statement of existence of certain class of processes, namely those that allow you to interconnect any two states of any system. And remember, we mean a well-defined system, separable in the sense that we have made very explicit.

The second assertion allows us to introduce a property, a general property for any of these systems and for any of its states by supporting the measurement procedure. That implies finding a weight process that interconnects two states. That way you can measure the energy difference between those two states. And that is what defines the property energy.

And then this property can be proved to be additive, to be transferable between systems as a result of interactions, and also to be conserved, which takes us to the idea of making a balance of this property, checking in a given process that the change in the value of the energy, so the difference between the final and the initial energy, that's the change in energy, be equal to the energy that has been exchanged during this process between the system and the environment, positive if received. And this is, of course, the hinge of the solution of many problems that you have certainly seen in the undergraduate or previous graduate courses on thermodynamics. So I rely upon your experience here because this is, as you know, not a course about applications or problem solving.

I assume that you have some experience of that. Because the more experience you have, the more your intuition and your sense of things will allow you to pick up the meaning of the underlying theory and assumptions that you are actually making when you perform, for example, an energy balance. Then we moved on to the second law. Also, the second law is made up of two assertions.

One is a statement of existence again. But now, this time it's the existence of the stable equilibrium states of a system. And that by itself, together with the definition of stable equilibrium state, remember, it's a state that cannot be changed without leaving some net external effects to your-- so in the environment of your system. So if your system is in a stable equilibrium state, in order to change it to another state, you have to spend something. You have to leave some net effect in the environment. Otherwise, it is impossible. And this impossibility is what allows us to prove the impossibility of a perpetual motion machine of the second kind, which is the Kelvin-Planck statement of the second law.

The second assertion supports the definition of a property that now we know, because we've defined it the last time, is entropy. So it assures that-- it says, well, you can always make a reversible weight process, which takes your system from any state it is in, to a stable equilibrium state. But not only a stable equilibrium state. A stable equilibrium state that, for example, could be in mutual equilibrium with your reservoir.

So in this picture, I jumped to this conclusion that we have used and proved as a consequence of the assertion two, the second law, and that we used as a means to define the measurement procedures for a property that we call temperature of a reservoir. I'm not going to repeat that. But as you have seen in the first homework set, I am asking you to repeat it in a short video.

And we used that same process, reversible weight process between the system and the reservoir, in order to measure the property entropy, which is defined by this ratio. It's the ratio between the change in energy of the reservoir that occurs when you manage to make this reversible weight process that interconnects-- in which your system goes between the two states for which you want to measure the entropy difference, divided by the temperature of the reservoir, which was defined by the previous measurement procedure. This ratio turns out to be independent of the reservoir that you have chosen and used as therefore just an auxiliary system, auxiliary to this measurement procedure. But the result is independent of that system.

Therefore, it is a property for just system A, something that depends on your system A, that we call the entropy. We also defined a property called available energy with respect to the reservoir. It is an additive property. It can be expressed in terms of energy and entropy. And it allows us to give an engineering interpretation of entropy as being, apart from a constant value, which is this group here.

It's proportional through the inverse of the temperature of the reservoir to the energy that is not available. So it's not transferable to a weight in a weight process for the system when in combination with the reservoir with the temperature. So entropy is the nonavailable energy. And it is additive. The additivity, remember we also had another property, which is adiabatic availability which contains much of the information and much of the value in terms of, what's the best I can do with a given system in a given state if I constrain myself on just weight processes? But the disadvantage of the adiabatic availability, is the fact that it is not additive.

Whereas entropy allows to compute the same things, and it is added, which is much more convenient. And then we moved, we also proved, or said that we can prove, this theorems about criteria to determine whether a weight process is reversible. And remember the definition of reversibility, a process is reversible if we can undo not only what happens to the system, but also what happens to the environment. So we have to be able to find some other process, not necessarily tracing back, going backwards, the original process, but one in which you can bring your system back to its initial state while also you bring the environment back to its initial state.

That definition is very solid and conceptually valid, but it is also very abstract. It doesn't correspond to a practicable procedure to determine whether a process is reversible or not. Because if you go by that definition, you are supposed to try all possible processes until you are really sure that you tried them all. And it's impossible to, or possible to bring back those states to their originals. And so that's clearly impractical.

Instead, property adiabatic availability, or entropy, or also available energy allow you to, if you know how to measure it, and we know because now we have the measurement procedures, they allow you to have a quantitative criterion to decide on the reversibility. And actually, you can also quantify the irreversibility in terms of how much these properties that appear in the criteria change. So in a reversible process, and remember, here we are talking about weight process, just weight process. In a reversible weight process, the entropy remains constant.

In an irreversible weight process, the entropy increases. That, together with the fact that entropy is additive, that entropy can be exchanged via interactions, you can transfer entropy from one system to the other. It's something that you do. Remember the example of the can of Coke in the refrigerator?

Well, when it cools down, there is not only energy that goes out of the can into the air of the refrigerator, but also, entropy flows. And we will get to that. And together with that, and with the principle of entropy non-decrease, which is in weight processes, which is just what we said about criteria for reversibility or irreversibility, you can write the entropy balance equation, which contains three concepts. On the left-hand side, the change in entropy during a given process for your system A, so the difference between the final and the initial entropy.

On the right-hand side, you have two contributions that must balance the left-hand side. The first contribution is how much entropy you have exchanged between your system and its environment during the process. And that is positive if received. So you have to put it positive if received. That's the meaning we've seen of the arrow on the symbol on the energy transfer.

And the second term is the entropy that has been generated by irreversibility. So it's the contribution of the irreversibility. So if the process is reversible, that term is equal to zero. Of course, we will return to energy and entropy balances.

And as you know, if you have done in previous courses, or maybe in energy conservation, or energy technologies courses, if you've done exergy, you know that the combination of the energy and entropy balance gives you exergy. Exergy, meaning the maximum useful effect that you can obtain under given conditions from a system in a given state, or vice versa. It's also, so by the combined energy and entropy balance, you can compute, what is the minimum amount of energy, so valuable resources, that you will have to spend in order to obtain a given effect, so a given change, for example, to produce or to heat up something, water, steel.

All right. And again, we'll come back when we talk about, in a couple of lectures, we will have one review of these exergy concepts. Then we moved on to focus on the equilibrium states, but not only the equilibrium states. Because here we have the maximum entropy principle that says that if you have your system, and you fix the values of the amounts of constituents, of the parameters of the external forces, such as the volume, but not necessarily only the volume. And you also fix the value of the energy, that fixes only a short part of the long list of values of properties that altogether form what we call the state of the system.

So by fixing this short partial part of the list, you're leaving free the rest of the properties. So there are many states that belong to that subset, so that share the same values of the amounts, the parameters and the energy. And among all these in this subset, there is one and only one stable equilibrium state, that is a consequence of the second law. But-- and another theorem is also that that stable equilibrium state has the highest value of the entropy. No other state has the same value. It has the strictly highest value within that subset.

And finally, we introduced the state principle, saying that, well, if it is true, like the second law says, that if I fix the values of amounts, parameters, and energy, and these values point to a unique, stable equilibrium state, it means that these values fix all the properties of that state. Because fixing the state means fixing the values of all the properties. So it means that for the category, for the very particular class of states, which are the stable equilibrium states, the properties are all functions of these three groups, amounts, parameters, and energy of these three properties, or it's actually r.

If you have r constituencies, r values, it's as many parameters as you need, plus the energy. So r plus s plus 1 values fix the value of any other property of the stable equilibrium state, including the entropy. So that gives a proof of the existence for stable equilibrium states of this function, which we call the fundamental relation. And which, if it is sufficiently regular or well behaved so that you can take derivatives, and these derivatives are not zero or infinite, you can invert this function.

So instead of writing S as a function of E, n and beta, you can write it as E is a function of S, n and beta. Whereas the fundamental relation in entropy form, this one, is always there for all systems, the E versus S, so the energy form, is there only for systems for which these derivatives don't go to zero. And therefore, we will see in a moment that there are some exceptions, particular systems that are important in the quantum world for which there is an upper bound in the energy.

Now about taking derivatives, when I have a function, I can write a differential of the function. We just do it just for one variable, or say, two variables. So z is a function of x and y, and therefore, the differential is the partial of f with respect to x times dx, plus the partial of f with respect to y in the dy. Now we apply here the idea to the function to the entropy form of the fundamental relation, and so written this way.

Really, here what I have is that the partial derivative of S with respect to E that multiplies dE, plus the partial derivative of S with respect to V, the second variable, times dV, plus the partial derivative of S with respect to n o ni times dni, and so on for all the other variables. We have defined those partial derivatives. Look at this one.

The partial of S with respect to E, we called it 1 over T because we will identify. So the inverse of that partial derivative is the temperature of the stable equilibrium state. This property, notice that is defined based on the fundamental relation. And the fundamental relation is defined only for the stable equilibrium state. So temperature is defined only for the stable equilibrium states.

Even for the reservoir, we define temperature in that particular way. And it's the temperature of the stable equilibrium state of the reservoir. Then, we give also names, for example, the partial derivative of S with respect to the volume, we call it p over T, where p will be identified as the pressure.

And the pressure, I think I will not go into this proof, but you can prove it. And again, you find the proof and all details in the book. If you haven't seen it, it's useful to go and look it up.

The pressure,-- when a system is-- first of all, is defined only for stable equilibrium state. And you say, well, look, if I have a wall, and I put a pressure sensor on the wall, I can always measure the pressure, even if my system is not in a stable equilibrium state. Well, no. What you're measuring then is the force per unit area on that location. So the force per unit area, you can always measure with the sensor that, we shouldn't call it pressure sensor. It's called force per unit area sensor.

It turns out that when the system is in a stable equilibrium state, that force per unit area corresponds to the pressure we find this way. But, for example, in a non-equilibrium state, when you measure force per unit area in different locations of your system, you may find different values. Whereas if your system is in a stable equilibrium state, wherever on the surface of the confining surface of your system you measure force per unit area, you find always the same value. And that's-- which corresponds to the pressure, so to give that-- to fix ideas.

Suppose I have a box. And in my box I got some particles. And suppose that the particles are initially all very regularly distributed only in this central part of the box. And they all move in one direction initially. So they're going to bounce on this wall, and then go back, and so on.

But, of course, due to some randomness that results from their collisions with the wall, eventually they will scatter around and fill the entire box. But initially, if you measure force per unit area here when the particles are hitting this wall, or here, you're going to find a very different value from what you do if you measure your pressure there. And by the way, what do you mean by measuring pressure? A pressure measurement is simply that you are conceptually breaking the wall, substituting it with a movable piston, and then find what force you need on that little piston of area a, small a, a small area, in order to keep it in the same place where the wall is.

Once you find this value of force, then the force per unit area is Fa over a. And that's the result of your force per unit area gauge or measurement device. But if you do that here, well, there are no particles sitting there, you find zero force per unit area. And as the particles scatter around and distribute, and become all randomly directed, then eventually, you will reach the stable equilibrium state. And in a stable equilibrium state, you will find the same values, no matter where on the wall of your system you're going to measure the force per unit area.

And in that limit, so for the stable equilibrium state, you will find that F over a at stable equilibrium is equal to this p, The thing that we call pressure of the stable equilibrium state. And these other derivatives, partial derivatives of the fundamental relation, but partial of S with respect to the amounts of constituents, are, if you change sign and divide by T, that's the chemical potential of that particular constituent.

We'll return to that, and also to a measurement device that is based, again, on measuring force per unit area, but not directly like this, but indirectly by putting a semipermeable, substituting the wall with a semipermeable membrane, and then measuring the force per unit area here, where just particles of one type can cross the semipermeable membrane. That will be a measurement of what we will call and what defines the partial pressure of constituent i. You measure it, again, by using this pressure of force per unit area gauge.

So back to the differential of the fundamental relation. So essentially, it's this formula, except that for the partial derivatives, we've given names. And we'll see at the end of today why we give names to these partial derivatives, because they enter into the necessary conditions that must be satisfied in order for-- when two systems are in mutual equilibrium. And these conditions will involve these partial derivatives. And these conditions will be consequences of the principle of maximum entropy that we just reviewed.

Now if you do the same development, so you write the differential of the fundamental relation, not in entropy form, but in energy form, so the same expression that you sort of invert, then you write the differential in this way. You can see it directly by solving the above equation for dE. So you take dE on the left-hand side and put the rest on the right-hand side, and you can obtain this equation. It's just algebra.

In this particular form, which is called the Gibbs relation, you see that temperature, pressure, the negative of the pressure, and the chemical potentials are the partial derivatives. Why do I say that? That's because the expression for the differential geometrically is related to-- if I have a surface and I focus on one point.

So suppose this is an equilibrium state and I'm talking about a surface. So if this is x, y, and z, and this surface has a function f of x, y equals z. So now I'm at a particular point, let's say, with x tilde for variable x, and y tilde for variable y. And therefore, that would be z tilde, so that particular stable equilibrium state.

Now writing the differential means writing the equation of the plane which is tangent to the surface at that point. These partial derivatives are the slopes of that plane in the directions of x and y. Now if I rewrite this function as a function, so I rewrite it in terms of changing dependent variables, so I solve it, make x explicit. So it becomes x going to be a function, say, of g and z. I'm sorry, a function g of z and y. So y remains an independent property, and now z becomes.

So it's a different function, of course. That's why I write f and g, but it's the same surface. So we can represent the same surface either in this way or in that way. And the tangent plane, therefore, hasn't changed, doesn't depend on how I decide to consider x, y, or z with a pair of them independent and then the other independent.

So the expression for the differentials should be the same geometrically, in the sense that they should represent the same. Therefore, if I write the differential of this function here, dx, the partial of g with respect to z in dz, plus the partial of g with respect to y in dy. But I can solve this equation and write it as dz equals 1 divided by the partial of g with respect to z times dx plus-- actually, minus the partial of g with respect to y, divided by the partial of g with respect to z times dy.

So I found either this or that represent this tangent plane. But also, this other form represents the same tangent plane. Therefore, I can conclude that this coefficient of dx in the expression of these-- if you compare this and that, these coefficients are equal. So this is equal to the partial of f-- oops. The partial of f with respect to x.

And this is equal to this. Same plane means same slopes, same coefficients. Therefore, this is the partial of f with respect to y. Of course, this is true only when f and g are related by the fact that one is the inverse of the other. And that's why-- that's what I've applied here to show that if that relation is 1 over T, its inverse is the derivative.

It is equal to the inverse of the derivative of g, which is the energy form, with respect to entropy. So you go from here to there using that form. Now it immediately stands out, the fact that if you deal with equilibrium states, stable equilibrium states, and there is an entire long chapter about relations that you can prove between properties of stable equilibrium states, we just touch on this and it's not our main concern. But you may find lots of papers, lots of formulas. And we will use them only when we need them.

But one thing I need to use because that would introduce and to, therefore, define, it's the symbol that we use. We use here a symbol. We just don't write only the partial derivative, but we write also parentheses and some subscripts. Why do we do that?

We do that because it could happen that, for example, all right, we have the fundamental relation in energy form written this way. But, for example, later we will give a brief-- we'll touch on the subject of changing variables. For example, because maybe entropy is not that easily measurable in the lab, in the sense that we don't have an entropy meter, but we have a thermometer.

So we measure entropy indirectly using the instruments that are simpler, like the thermometer. And the thermometer we will see measures the property temperature, which is the partial of this function with respect to the first variable, as written here. So why do I put the n and V there? OK, because, you see, the next thing I do, I can do is, for example, to write an expression of how the energy changes. Let me call it E tilde, as a function of T, V and n.

See? So now I look at these two expressions. They're different functions. But, for example, suppose I'm interested in the pressure. I take the pressure. It's minus the E, the partial of E with respect to V of the fundamental relation of this formula. But now that I have another function that expresses the energy in terms of other variables in which I also have volume, I may be curious to see, well, how about doing minus the partial of E tilde with respect to V? Is that the pressure?

Well, not necessarily. And actually, no. And sometimes if I'm sloppy and maybe I say, all right, this is the function I'm interested in. I don't want to carry around the tilde, so I just write it as E. Well, then I may get confused. Because when I look at this one or look at that one, which is which?

So the idea is, if you want to be careful, is to carry with your partial derivatives also a precise memory or indication of what the other independent variables of your function are. So if I write here the other variables, so I write S and n, and here I write the other variables, which are T and n, there is no way I can get confused. Because by just looking at the formula for the partial derivative, I know also what were the original variables of the function of which I'm taking the derivative.

So this is a notation to avoid to get lost and confused. And this kind of confusion is very common if you don't-- because many times, maybe you don't need this kind of pedantic way of proceeding because the context may be enough. If below is just below that, writing that partial derivative, you have a paragraph that says, well, this is the equation of which I'm taking the derivative, then you're OK. The context tells you what is the derivative of what.

But if, in more complex situations, where you keep changing variables, then this is really essential. And that's why in the business of thermodynamics it has been introduced and it is standard. So also, to be sympathetic with mathematicians, this, you should not read this symbol as saying, the derivative of energy with respect to volume at constant entropy and amounts of constituents.

Yeah, you can say it. Many people say it. Sometimes I even say it, but I don't mean it. Yeah. The real meaning of this is that these are the independent variables. So I'm taking the partial derivative of a function, the partial derivative with respect to volume of a function of energy, volume, entropy, and amounts of constituents. That's the proper language.

Why do we give names to temperature, pressure, and then chemical potentials? Because they enter, and we will see it hopefully later today, not sure. Any way, because they enter in the conditions for mutual equilibrium between systems.

So we'll return to these to make some proofs, but just to anticipate, when two systems, A and B, are in mutual equilibrium, it means that the overall system is in a stable equilibrium state. That's the definition of mutual equilibrium, remember. So we will prove and we will actually-- I want to go over these proofs because they're useful also for other reasons.

It turns out that if the two systems, A and B, can exchange energy, then they must, if they are in mutual equilibrium, they must have the same temperature. So the temperature of system A of the stable equilibrium state in which system A is must be equal to the temperature of the stable equilibrium state in which system B is when they are in mutual equilibrium. They can also exchange volume, for example, by means of a movable piston or a partition.

There is a system, as the piston moves, you see that, for example, it moves to the right. The volume of A increases, that of B decreases by the same amount. So you can say that the piston-- you can interpret it as the piston has allowed the systems to exchange volume. One gains the volume by subtracting it from the other. So it's like a transfer of volume.

All right. In that situation, in order for the two systems to be in mutual equilibrium, you need also pressure equality. If, instead you have a porous wall, or a semipermeable membrane that allows the exchange of one of the constituents between system A and system B, well, the necessary condition for mutual equilibrium is equality of the chemical potentials of that constituent. So the chemical potential of constituent i measured in system A must be equal to the chemical potential of system B, measured in system B.

So we will prove this because these are very important. And actually, regarding equality of chemical potentials, we will go a long way in finding very interesting results and important results for applications. But before we go and prove these conditions for mutual equilibrium, I promised that I would review what we have done so far.

You may call it thermodynamics without heat so far by introducing this energy versus entropy diagram representation of states, which is so important that we put it in the cover of our book. OK, this is the surface. This is a fundamental relation for water.

All right. So how do we get to construct these energy versus entropy diagrams? Again, we start from the idea of state. A state is a long list of numbers, usually very long. We define a few of-- now these numbers are the properties, are the amounts of constituents, the values of the parameters, but also, all the properties of our system at the given instant of time.

Among these properties, we have energy and entropy, but we have also many other. So in order to have a complete representation, geometrical representation for a state of a system, you would need a multi-dimensional space in which we have one axis for each of the independent properties of your system. And since the independent properties of a system are generally very large, or even most of the times infinite, then you need to simplify.

So what we do is to project onto a plane. But first, what we do is to make a cut of this multi-dimensional space, a cut at fixed values of the amounts of constituents and the parameters. When I say parameters, think of the volume. And that's the most common, at least when you study properties of substances.

So if I fix the values of the amounts and parameters, I still have a large subset. I still need a multi-dimensional space, only its dimensions is the full thing minus the number of constituents and the number of parameters. Still very large. Then, you project all the states onto the plane made of the two variables that we most like, energy and entropy.

And then you get a 2D representation, and it is going to look like this. Energy and entropy. You project-- So let's look at the generic point here. The generic point here, remember, is the projection onto that plane. Many states will project onto that plane because many states will share those same values of energy and entropy but differ in the values of other properties. So they are different states which, nevertheless, are represented by the same point as a result of the projection.

Now that we have understood the geometry, let's see what the theorems that we have seen so far tell us about where these states can be in this diagram. So for example, let's start with a statement of the first assertion of the statement of the second law. It said, we'll consider all the states of the system with a given value of the energy.

So fix the value of the energy. All the states will collapse or will project onto this dashed line, horizontal. And you see we have the maximum entropy principle that we just mentioned. It says that among all these states, there is a stable equilibrium state, which is the one that has the highest value of entropy. There are no other states with that value or even higher values of entropy.

So that means that there is a maximum for the entropy for that given value for the energy. And corresponding to that maximum, there is one state. Notice it's only one state. So this particular point here is the projection of only one state, whereas here it's a projection of many states. When you go to equilibrium, there is only one state.

Well, that's to say that geometrically, this curve, which is the locus of all the stable equilibrium states, is a sort of a wire curve in that multi-dimensional space. All right. So there are no states with higher entropy. So all the possible states are to the left with a lesser entropy than the stable equilibrium state.

I do the same for another value of energy and I get another stable equilibrium state. I do it for the minimum value of energy compatible with the fixed values of amounts of constituents and parameters that we have chosen in order to make our cut of the multi-dimensional space. And we still have a stable equilibrium state. And that's the minimum energy stable equilibrium state. We'll come back to this in a moment.

The slope of this curve, you see it? This curve represents the stable equilibrium state fundamental relation in energy form, because it's E is in the ordinates and S in the abscissa. And so this curve is the representation of E versus S at fixed the values of n and V.

So the partial derivative of this function corresponds to-- it's this thing. It's the temperature, or actually, partial derivative is the slope of the tangent to the curve at a given stable equilibrium state. So the temperature is the angular coefficient of the tangent line, the slope, the temperature.

So I can read the temperature, and I have built in this diagram also a result that we haven't proved yet, namely the concavity of this fundamental relation, implying that as you go high in energy, so you go stable equilibrium states with higher energy, the slope goes up. They also have higher temperature. So temperature is an increasing function of energy.

But remember, temperature is defined only as being the slope of this curve, only for the stable equilibrium state for which there is a curve. You are inside here. There is no fundamental relation. There is no function to take derivatives. There is no temperature.

Yeah, maybe you can compute things like the average kinetic energy of the particles. But whereas this is related to temperature at stable equilibrium, it is not temperature if you are off equilibrium. Of course, for stable equilibrium states-- all right. Yes, as I go down in energy, I reach the minimum energy stable equilibrium state.

And these here, I have built in another feature that goes by the name of the third law of thermodynamics that says that the lowest energy stable equilibrium state has zero temperature. We will not prove that as this comes more from the models of statistical mechanics or quantum mechanics. So we have nothing to add to that important but very well known result. It comes from physics.

In a moment, we will also see, but I can anticipate that the entropy takes a minimum value. And the minimum value is for those particular non-equilibrium states for which the adiabatic availability is equal to the energy, or better to the difference between energy and the minimum energy allowed for that given combination of amounts of constituents and volume. So if I have a state here, this state-- from this state, you can transfer in a weight process to the weight, you can extract out of your system in a weight process all the energy of the system, meaning that you can take that state and bring the system down to this state, the minimum energy.

You can do this here and you extract this much energy. Whereas in a moment, you'll see that if you do that in a non-equilibrium state, the adiabatic availability corresponds to this much. You can go at most down to this stable equilibrium state.

And if you start from a stable equilibrium state, remember what the theorem about impossibility of perpetual motion machine of the second kind says. There's no way you can start from an equilibrium-- from a stable equilibrium state and extract energy in a weight process. And here it is. You cannot go down in a weight process.

You see in a weight process the feature is that if you want to go down in energy here, you need to also reduce the entropy. But you cannot reduce the entropy in a weight process. We'll return, of course, into these ideas.

Here I just wanted to say that there are some special systems for which there is an upper bound to the energy. These systems are those that do not have translational, or rotational, or vibrational degrees of freedom. Because if you have a translational degree of freedom, a particle can move. If it can move, you can accelerate it to as much velocity as you wish.

Yeah, there is the limit of the speed of light, and so on. Maybe that is an upper bound. I've never really thought about that. But here we are talking about systems like the spin of an electron. So if you want to concentrate on just the spin feature of an electron without all the other details so that the electron must not be bound in an atom and so on, but if you can define a system in which the only aspect that you are interested in is the spin, or if you don't like the spin, it could be the polarization of photons.

It's very typical of quantum optics because with lasers and so on you can produce very diluted beams with photons, like you can treat one photon one at a time. And you can, using particular filters, when you produce these photons, you can have them polarized in various ways. But these various ways are finite. So the spin or maybe even an atom can be modeled with a finite number of energy levels. And if it's finite, it means that the energy cannot go above the upper energy level.

Well, in this situation, the stable equilibrium state fundamental relation looks like this when you project on an E versus S diagram. This is the fundamental relation that you obtain.

That function that you are representing there, let me write it as S is a function of E. So this is E minimum. This is E maximum. And the fundamental relation S as a function of E plus whatever other parameters and amounts are, looks like that.

All right. So yeah, nothing more. For systems with translational degrees of freedom, S versus E instead, there is a minimum. Particles are not moving. So there is no kinetic energy, and therefore, they are at minimum. And this corresponds to the zero temperature stable equilibrium state.

And then this is, well, the fundamental relation, the one that we have seen just in the previous diagram. But if there is an upper bound, you reach this value here and you will go down. So look at what happens to the slopes.

Here the slope is infinite. And remember that the partial of S with respect to E is the inverse of the temperature, 1 over T. So if 1 over T is infinite, the temperature here is 0. Then it reaches a maximum, the entropy reaches a maximum for a value of the energy. So we are moving-- this is 0 temperature reaches a maximum here.

Here, the inverse of the temperature is equal to 0 because the slope is equal to 0. So that means the temperature here is infinite. And then you go on the other side here and the entropy goes down. So you get another state with zero entropy, another stable equilibrium state with zero entropy corresponding to the maximum energy. The second law is still satisfied. For every value of the energy, there is one and only one stable equilibrium state.

You cannot do it the other way around. In other words, if I fix the value of the entropy, so the minimum energy principle instead doesn't apply in this case. In this case, it does. I fixed the value of the entropy. And the stable equilibrium state corresponds to the minimum energy because the possible states are only in this area here. And that's the minimum energy.

But for a special system like the one that we're talking about, I fixed the value of the entropy. And there are two stable equilibrium states, one with minimum energy and one with maximum energy. Except here, I fixed the value of the entropy. There is only one stable equilibrium state.

And if I fix a higher value of entropy than this one, there are no states. So also, this last stage, so like the third law says that there is 0 temperature for the minimum energy stable equilibrium state, it also says that-- implies, I mean, that the temperature of the highest energy stable equilibrium state is 0. However, here you have a little problem somehow of discontinuity because you go-- yeah, I forgot to say one important thing.

The slope on this side of the curve is positive, whereas on this other side of the curve, the slope is negative. So part of all these stable equilibrium states have negative temperatures. Negative temperatures are not so esoteric. They were discovered in, I think it was 1956, that's when I was born, by Ramsey at Harvard, just next door.

Actually, his daughter was the wife of Professor Keck, who was downstairs, and with whom I have done my master's thesis. All right, so negative temperatures. We will see that the idea of negative temperature, the name is not really very good.

As you say, negative. It's below zero. Well, really, actually, if temperature measures the tendency of a system, as we will see, to yield energy, to give out energy, these negative temperature equilibrium states have more tendency to give out energy than the positive temperature equilibrium states.

They are hard to keep also because we-- I don't know if we can make in a lab something that has the properties of that we could call a reservoir. Although I'm not sure, but that we could call a reservoir with a negative temperature. I'm not sure it can be done in the lab simply because most of the times reservoirs have been constructed by using systems that have translational degrees of freedom. And therefore, they have no negative temperatures. But maybe it is possible also to do a reservoir with negative temperatures.

Anyway, so we have a problem here that the temperature goes from zero positive values to plus infinity here. Then, immediately after it switches to minus infinity and it goes down to zero again. So there is some sort of discontinuity if we insist in talking of temperature.

But if instead we look at a scale in which we, instead of temperature, we do minus 1 over temperature, this, which can be interpreted again as the tendency and escaping tendency for energy. It still measures the energy-- the tendency of a system to, in a stable equilibrium state, to give up energy. And you see then this property here for this curve would go from minus infinity in the minimum energy, minus infinity, then goes to 0.

And from 0 without discontinuities, it goes to plus infinity. So that is also a better scale. So it also shows you that this property is continuously increasing from minus infinity, through 0 to plus infinity. And these ones that have high value for this property are the hotter, if we understand as hot something that has a strong tendency to give out energy.

So this much for the special systems. Now let's go back to our E versus S diagram and try to visualize the idea of adiabatic availability. Remember, the adiabatic availability is the property that measures the maximum amount of energy that you can extract out of a system in a given state in a weight process.

And you manage to extract it when you manage to take your system. Yeah, there is a y there. That's a wrong spelling. That's Italian. It's also wrong in Italian. Anyway, I'll correct it. It has to finish to end up in the stable equilibrium state. And that process must be reversible.

OK, so what do we know of a reversible process or reversible weight process in terms of entropy? What did we learn? We call it the principle of entropy non-decrease. But we call it also criterion for reversibility of processes. If a process, a weight process is reversible, the entropy stays constant.

So let's do this in a plot. I start from my system in some state here, generic state A1. I make a process in which I want to take energy out of the system. So the energy goes down because I'm taking out of the system. It goes down because I want to give it to the weight.

I want the process to be not only weight process, but reversible. So in a reversible weight process, the entropy doesn't change. So I go down this way. I go down until there are states. Eventually, I reach the minimum energy stable equilibrium state with that entropy. And there are no more states below that.

So that's all I can do in a reversible weight process. This is as much as I can go down. So the difference between the original energy and the energy of the lowest energy stable equilibrium state with the initial entropy is the adiabatic availability. So this is the visualization of the adiabatic availability. It's the distance in that diagram between your state and the stable equilibrium curve vertically.

So, for example, if I consider-- if my initial state were here at 0 entropy, you see I can go down and meet the zero entropy stable equilibrium state, which is the minimum energy stable equilibrium state of mechanics, or actually, regarding this area, it's used. It's discussed in the book. I don't want to go into the details, but somehow the stable equilibrium state is not necessarily 0 entropy.

It's 0 temperature by the third law, but it could have a finite entropy equal to the logarithm of the degeneracy of that lowest energy or ground state. Nevertheless, the amount of the adiabatic availability for a state with 0 entropy is equal to the difference between its energy and the lowest energy for those values of amounts and parameters. So this is the visualization of the adiabatic availability.

For a given energy, the more I go to states that have higher entropy, the less adiabatic availability they have, until I reach the stable equilibrium state that has 0 adiabatic availability. I'm already there. It cannot go down vertically because there are no states available there.

We talked about reservoirs. Remember, reservoirs have a constant temperature. Their stable equilibrium states have all the same temperature, TR. For as long as the system behaves as a reservoir, because, as we said, if I make a reservoir with-- yeah, if it's done like water at the triple point, as long as I have all the three phases coexisting that behaves as a reservoir in stable equilibrium states.

But if I put too much energy, for example, and one of the phrases disappears, then that system doesn't behave as a reservoir anymore. So it's in a limited range of states the system can behave as a thermal reservoir or can approximate, because that is an approximation practice. Because rigorously speaking, a true reservoir doesn't really exist.

I know I'm confusing you, but sometimes it's good to be confused. Because a reservoir is a very limiting system. And in fact, if you think deeply enough, and you'll find also this discussed in the book, you'll see that, strictly speaking, if a reservoir satisfied its defining features, it would be violating the second law. So we are using that as a limiting system.

And this, in fact, allows me to say that in the years after publishing that book, we've been together with Professor Zanchini of the University of Bologna in Italy, who contributed also in some of the proofs of the book. We went on and tried to find an alternative way of defining entropy, without the reservoir. Because the reservoir is some sort of a macroscopic object. And we wanted to do it more generally so that our definition of entropy could extend also to microscopic situations, but also in an operational, therefore, laboratory applicable measurement procedure.

So we did. We have some papers around that concept. And also, a famous mathematician, Lieb, later on after our book was published, alternative definitions of entropy valid for non-equilibrium states. And initially, they didn't do it for non-equilibrium states. But then they realized that they could do it, and that we were sort of doing the same thing.

So what I'm saying is that I'm telling you this definition of entropy, as it were an easy stuff, but it's not really very easy. Because conceptually, entropy has always been a difficult topic to understand. It has so many facets. One is the laboratory. The other is the statistical. And now we have also the quantum. So it has so many facets that you shouldn't say, yes, I understand what entropy is.

On the other hand, you should say that you understand what entropy is. You know, I like contradicting a bit. Because if you want to go home now and say, well, what did you learn in the thermodynamics course so far? Well, I learned you could say that, yeah, there is energy. Everybody knows about energy. With energy, you can do useful things.

But not all the energy is convertible into useful effects. In fact, entropy is a measurement of that part of the energy that cannot be converted into useful effects. So from an engineer point of view, that's a very clear statement, and it's true. There's no controversy about this.

All right, so let's move on because we are running out of time. And so the reservoir has stable equilibrium states that all have the same temperature. So since temperature is the slope of the fundamental relation-- of the curve that represents the fundamental relation, the fundamental relation for a reservoir is a straight line. So the equation for a straight line is this one.

Changes in energy are related to changes in entropy between two. If the system goes from one stable equilibrium state to another stable equilibrium state, and therefore, it moves along this curve, then the ratio of the energy change to the entropy change is equal to the temperature of the reservoir. Why we use the reservoir? Remember we use it so that we could make that property additive.

So we built additivity into the concept of adiabatic availability. And in fact, if we consider the adiabatic availability of a composite system, composite of a system like a normal system, and the reservoir, then the adiabatic availability of this situation is what we call available energy. It turns out to be a property of system A with respect to a given reservoir. It's called available energy of a system with respect to a given reservoir.

And we have given the formal expression in terms of energy and entropy. So you can compute the available energy. The maximum work that you can extract from your system A when it has available the possibility to interact with a reservoir and exchange with it.

So let's see how we could construct. See, this is the formula for available energy. And how can we construct that formula? So here is the E versus S diagram for our system A. Fixed values of n and V. Stable equilibrium state curve.

Then we consider, again, state A1. If, for state A1, I make a reversible weight process, the entropy remains constant, and I can go down this much. And that's how I extract the adiabatic availability.

When I want to extract the available energy here, remember in the end, in the final state, the composite system must be in a stable equilibrium state. It's only then-- it's only when I reach the stable equilibrium state that I cannot extract any more in a weight process. So stable equilibrium state for a combination means mutual equilibrium. So the final state of system A is in mutual equilibrium with the reservoir.

If the reservoir is a temperature TR, when the system A is in mutual equilibrium with the reservoir, we said that we will prove that the two systems in mutual equilibrium must have the same temperature. So system A must end up in the stable equilibrium state that has a slope-- that has temperature equal to the temperature of the reservoir. So, if is this the temperature of the reservoir,

I go and look for the point here on this curve where the slope is equal to TR. That is the state in which system A will be in mutual equilibrium with the reservoir. And that is going to be the final state of system A. You see?

In order to go from the initial state of system A to this final state, I need to change the entropy of the system. In this case, since state AR is to the right in the diagram of state A1, the entropy SR is greater than S1. And one possibility is to let entropy increase by means of some spontaneous process that make a weight process an irreversible weight process.

In an irreversible weight process, I can increase the entropy. And so I can go from here to there in a weight process. And the amount of energy I would extract in that weight process would be only the difference between the initial and final energy. That's the energy balance. So I would extract only this much.

But another way is to-- since I need this entropy in order to go from here to there, I can ask it to the reservoir. The reservoir is there and interacts with my system in whatever way is allowed. So they can also exchange entropy.

So if I ask the reservoir to give me this much entropy so that I can go from here to here in the entropy axis, the reservoir-- let's go back to the-- so if the reservoir has to give me some entropy, it means that it must go from here to the left. In order to give me some entropy, it can give me also some energy. So I say, all right, reservoir, while you are giving me this much entropy in going from here to here, you can give me also that energy.

You can go from this stable equilibrium state to this lower energy stable equilibrium state. And that energy becomes available to go to the weight. So you take energy out of the reservoir and give that energy to the weight, and give the entropy to the system.

And therefore, you can see this inclined line. You can view it also as the stable equilibrium state curve for the reservoir. So this much energy reduction for the reservoir implies this much energy. So this much entropy reduction implies this much energy reduction.

So in addition to the energy that you can extract directly from system A going from here to here, the difference between initial and final energy of system A, you can add also this much as energy that is extracted from the reservoir. And therefore, geometrically the available energy is the sum of these two contributions, which is also the geometric representation of this formula. All right.

Well, I think we will take it from here. I want to skip this for the moment. And so the next time I still have to do what I didn't manage to do today. It's the necessary conditions for mutual equilibrium. So I think, yes, time is up for today. So I'll see you on Friday.